

(12) **UK Patent Application** (19) **GB** (11) **2 364 322** (13) **A**

(43) Date of A Publication **23.01.2002**

(21) Application No **0016270.1**

(22) Date of Filing **04.07.2000**

(71) Applicant(s)  
**Ilford Imaging UK Limited**  
(Incorporated in the United Kingdom)  
Town Lane, Mobberley, **KNUTSFORD**, Cheshire,  
WA16 7JL, United Kingdom

(72) Inventor(s)  
**Peter Edward Rose**  
**Malcolm David Tirel**

(74) Agent and/or Address for Service  
**Ilford Imaging UK Limited**  
Town Lane, Mobberley, **KNUTSFORD**, Cheshire,  
WA16 7JL, United Kingdom

(51) INT CL<sup>7</sup>  
**C09B 29/33, C09D 11/02**

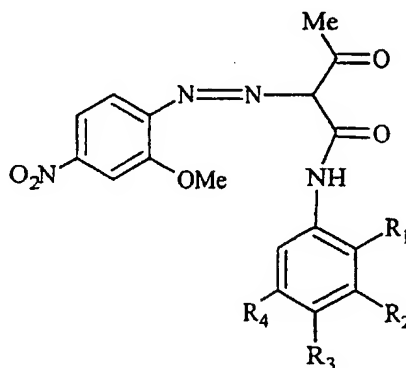
(52) UK CL (Edition T)  
**C4P PAC02 PAM12B PAM28 PAM34K PAZ PAZ01B**  
**PT03 PT08 PT09 PT11 PT14 P110**  
**U1S S1390**

(56) Documents Cited  
**None**

(58) Field of Search  
**Online: CAS ONLINE**

(54) Abstract Title  
**N-(sulphophenyl)-alpha-(2-methoxy-4-nitrophenylazo)acetoacetamides and their use in pigment & ink compositions**

(57) There is provided an azo compound of formula I



in which the groups  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are individually hydrogen, a sulphonic acid group or salt thereof, a carboxylic acid group or salt thereof, a lower ( $C_{1-4}$ ) alkyl group, a halogen, a sulphonamide group, a carboxylic amide group, a nitro group, a group OX, or a group COOX where X is a lower ( $C_{1-4}$ ) alkyl group, provided at least one of the groups  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is a sulphonic acid group or salt thereof.

There is also provided a pigment composition which comprises a combination of a yellow monoazo pigment and a compound of formula I and an aqueous ink which comprises a combination of a yellow monoazo pigment and a compound of formula I. Preferably the pigment is CI Pigment Yellow 74.

Compounds of formula I are useful for improving the dispersion properties of pigment compositions comprising certain yellow monoazo pigments, including water based dispersions and formulations such as aqueous inks, especially ink jet inks.

This invention relates to novel chemical compounds and to the use thereof for improving the dispersion properties of pigment compositions. More particularly it relates to the use for improving the dispersion properties of aqueous compositions comprising yellow monoazo pigments and to the use thereof in inks.

#### BACKGROUND to the INVENTION

Pigments are colorants which are considered to be effectively insoluble in the application medium, and many such compounds are well known and in wide commercial use. Various classes of pigment are classified in the Pigments and Solvent Dyes section of the Colour Index International, published by the Society of Dyers and Colorists in 1997, and there are of course many other insoluble colorants which are not in this list. It is common practice to provide pigment compositions in the form of finely divided dispersions, which may be produced by well known methods such as ball milling or by the methods disclosed in United States Patents 5,026,427, 5,310,778, or 5,976,232. It is common to have present at least one dispersant or surfactant during the dispersion process in order to obtain the optimum dispersion properties, and it is well known that the choice of this dispersant is very important for achieving these properties. The purpose of the dispersant is to stabilise the particles and to prevent growth by aggregation or flocculation. The dispersant or dispersants may be incorporated into the pigment at synthesis or during an aftertreatment,

may be added before or during the dispersion stage, may be added to the final dispersion or formulation, or may be added in a combination of these ways. Suitable dispersants are well known and include, for example, resin polymers such as those disclosed in United States Patents 3,874,891 and 4,009,142, surfactants such as the phosphate esters of United States Patents 4,872,916 and 5,466,482, and coloured compounds such as dyes which are structurally related to the pigment in use. For instance United States Patent 2,816,045 discloses the use of salts of copper phthalocyanine sulphonic acids to improve the flocculation resistance of formulations comprising copper phthalocyanine pigments, United States Patent 3,386,843 discloses salts of sulphonated quinacridone compounds and their use for improving the tinctorial and rheological properties of compositions comprising structurally related quinacridone pigments, and European Patent Application 451094 and Japanese Patent Application 63 178169 disclose sulphonated diarylide azo compounds and the use thereof in combination with related benzidine type yellow pigments.

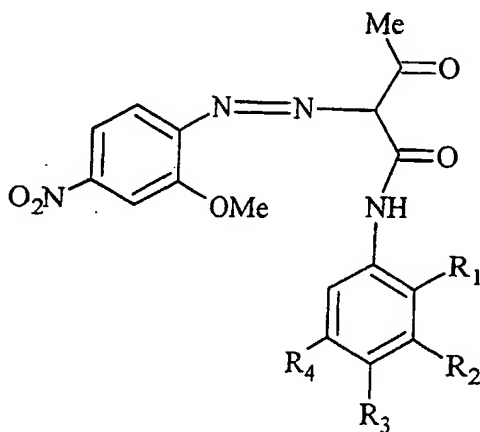
It is also known from Japanese Patent Application 05 117626 that cocrystals comprising certain monoazo compounds are useful as pigments.

We have discovered a new class of yellow azo dye which is useful for improving the dispersion properties of certain yellow monoazo pigments of wide commercial use. The compounds of this invention are particularly useful

for improving the properties of water based dispersions and of formulations such as aqueous inks based on them.

### SUMMARY of the INVENTION

According to the present invention there is provided an azo compound of general structure I:-



In which the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are individually hydrogen, a sulphonic acid group or salt thereof, a carboxylic acid group or salt thereof, a lower alkyl group, a halogen, a sulphonamide group, a carboxylic amide group, a nitro group, a group OX, or a group COOX where X is a lower alkyl group. By lower alkyl group is meant an alkyl group comprising up to four carbon atoms. At least one of the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is a sulphonic acid group or salt thereof. Preferably the others of the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are hydrogen, a halogen, or a methyl group, and most preferably they are all hydrogen. Preferably the sulphonic acid group or groups of the compound of formula I

are in the salt form. The compound of formula **I** may conveniently be synthesised in the salt form by suitable preparative conditions, or it may be prepared in the form of the free acid and neutralised for use by addition of a suitable base. Suitable salt forming cations for the sulphonic acid group or groups are alkali metal cations such as lithium, sodium, or potassium, alkaline earth or other metallic cations, an ammonium cation, or an organic nitrogen containing cation such as triethanolammonium, triethylammonium, or pyridinium.

It is to be understood that the compounds of formula **I** are written in the conventional azo tautomeric structure, but that they may exist partly or completely in alternative keto-hydrazone or other tautomers as is known for certain azo compounds (see for example the article by K.Hunger in Review of Progress in Coloration, volume 29, 1999 page 74). The formula **I** hence also embraces these other tautomeric structures.

Specific useful compounds of formula **I** include the following:

COMPOUND	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
<b>A</b>	H	H	SO <sub>3</sub> Na	H
<b>B</b>	SO <sub>3</sub> Na	H	H	H
<b>C</b>	H	SO <sub>3</sub> Na	H	H

Compounds of Formula **I** may be prepared by well known methods, and in particular by the standard synthetic route for azo dyes wherein a suitable amine is diazotised and coupled with the appropriate acetoacetanilide. The

substituted anilines and acetoacetamido benzene sulphonic acids required for the preparation of the compounds of formula I by this reaction are known compounds or may be prepared by known methods.

The compounds of the invention are useful for improving the dispersion properties of pigment compositions comprising certain yellow monoazo pigments and in particular for improving the dispersion properties of the yellow azo pigment catalogued by the Colour Index as Pigment Yellow 74.

It is common practice to provide pigment compositions in the form of finely divided dispersions in a suitable carrier or solvent, which may be produced by a dispersion stage subsequent to the synthesis of the pigment. According to a second aspect of the invention there is provided a pigment dispersion which comprises a combination of a yellow monoazo pigment and a compound of formula I dispersed in an aqueous solvent. By aqueous solvent is meant a solvent wherein the liquid phase is predominantly water, but which may also comprise in addition at least one water soluble organic cosolvent. The proportion of compound of formula I may be up to 100% by weight on the pigment, but is preferably between about 1% and about 25%, and most preferably between about 3% and about 10% by weight on the pigment. According to this aspect the sulphonic acid group or groups of the compound of formula I are preferably in the salt form.

According to this aspect it is preferred that the compound of formula I be added to the pigment at the dispersion stage. There may also be present in the dispersion at least one additional dispersant or surfactant. This additional dispersant or surfactant may be added to the pigment at synthesis, may be added as a grinding aid at the dispersion stage, or may be added after the dispersion stage. Suitable additional dispersants may include any of the dispersant types known in the art, but preferably the additional dispersant is a nonionic dispersant. There may also be present in the dispersion other additives as are known in the art such as, for example, one or more organic cosolvents.

A suitable concentration for the pigment in a dispersion is up to about 50% depending on the dispersing method and the end use. A concentration of about 10 to about 25% is suitable in most cases. If an additional dispersant is used then this may be present at up to 100% by weight on the pigment, but is preferably present at up to about 50% by weight on pigment.

According to this aspect it is particularly preferred that the pigment in the dispersion is CI Pigment Yellow 74.

According to a third aspect of the invention there is provided an aqueous ink which comprises a combination of a yellow monoazo pigment and a compound of formula I. According to this aspect the sulphonic acid group or

groups of the compound of formula I are preferably in the salt form. By aqueous ink is meant an ink wherein the liquid phase is predominantly water, but which may also comprise at least one additional water soluble organic cosolvent. The ink compositions of the invention may also contain other components which are advantageously added to aqueous inks, such as surfactants, viscosity modifiers, biocides, and metal sequestering agents. Such additional components are well known in the art.

According to this aspect it is particularly preferred that the yellow pigment in the ink is CI Pigment Yellow 74. Therefore according to this aspect there is provided an ink which comprises a combination of Pigment Yellow 74 with the compound of formula I. The proportion of compound of formula I may be up to 100% by weight on the pigment, but is preferably between about 1% and about 25%, and most preferably between about 3% and about 10% by weight on the pigment.

The aqueous ink compositions of the invention are especially suited to use in ink jet printers. According to this aspect it is preferred that there is at least one organic cosolvent present in the ink, and most preferred that there is a combination of cosolvents present in the ink. Suitable cosolvents are well known in the art, and include lower aliphatic alcohols and ketones, glycols, polyhydric alcohols, poly(ethylene oxides), glycol ethers, heterocycles such as dioxan or tetrahydrofuran, nitrogen containing compounds such as urea,

pyrrolidone, and alkyl pyrrolidones, and sulphur containing compounds such as sulpholane and thiodiglycol.

For this use, the concentration of the pigment composition in the ink is preferably between about 1% and about 8% and the concentration of organic cosolvents in the ink is preferably between about 10% and about 50%, and most preferably between about 15% and about 25%. It is preferred to prepare inks by dispersing the pigment in the presence of the compound of formula 1 in deionised water to provide a dispersion, and then to dilute this dispersion to form the ink by adding additional water together with the organic cosolvents and any other additives.

The following examples will serve to illustrate the invention.

Synthesis Example 1 - Preparation of compound A4-[[2-[(2-Methoxy-4-nitrophenyl)azo]-1,3-dioxobutyl]amino]-benzenesulphonic acid sodium salt.

Nitrosyl sulphuric acid (0.70g; 5.5mmol) was added portionwise to a chilled, stirred mixture of 2-methoxy-4-nitroaniline (0.84g; 5.0mmol) in glacial acetic acid (3ml), water (1.5ml) and 30% hydrochloric acid (3ml) whilst keeping the internal temperature below 5°. The clear yellow solution was stirred in ice for a further 90 min. This solution was then added dropwise, during *ca* 10 min, to a stirred, chilled solution of 4-acetoacetamidobenzenesulphonic acid sodium salt (1.39g; 5.0mmol) in water (35 ml), sodium hydroxide (1.0g), and sodium acetate (1.0g). The yellow-orange mixture was stirred for a further 1h, then heated at 90° (oil bath temperature) for 30 min. After the reaction mixture was allowed to cool to room temperature it was filtered, washed (water, acetone; ether) and dried to give a yellow solid, yield 2.11g.

This material was heated at reflux in methanol (50ml) for 90 min, filtered whilst warm, washed (propan-2-ol; acetone; ether) and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub> to furnish compound A as a bright yellow solid, yield 1.82g (78%), melting point > 360°,  $\lambda_{\text{max}}$  414nm.

C<sub>17</sub>H<sub>15</sub>N<sub>4</sub>NaO<sub>8</sub>S.0.5H<sub>2</sub>O Requires: C = 43.7%, H = 3.5%, N = 12.0%.

Found: C = 43.9%, H = 3.8%, N = 11.6%.

Synthesis Example 2 - Preparation of Compound B.2-[[2-[(2-Methoxy-4-nitrophenyl)azo]-1,3-dioxobutyl]amino]-benzenesulphonic acid Sodium Salt.

Nitrosyl sulphuric acid (0.42g; 3.3mmol) was added portionwise to a stirred, chilled mixture of 2-methoxy-4-nitroaniline (0.5g; 3.0mmol) in glacial acetic acid (2ml), water (1ml) and 30% hydrochloric acid (2ml) whilst maintaining the internal temperature below 5°. The yellow solution was stirred in an ice-bath for a further 30min. This solution was then added dropwise, during *ca* 10 min, to a stirred, chilled solution of 2-acetoacetamido benzenesulphonic acid sodium salt (0.83g; 3.0mmol) in water (30ml), sodium hydroxide (0.6g), and sodium acetate (0.6g). The yellow gelatinous mixture was stirred for a further 90min, then heated at 90° (oil bath temperature) for 90min. After cooling to room temperature the mixture was filtered, washed (little H<sub>2</sub>O; acetone) and air dried to give a yellow solid, yield 0.92g.

This material was heated at reflux in acetone (45ml) for 1h, filtered whilst warm and dried *in vacuo* over Phosphorus pentoxide to afford compound **B** as a yellow solid, yield 0.91g (66%).

Mp 320-3°,  $\lambda_{\text{max}}$  416nm.

C<sub>17</sub>H<sub>15</sub>N<sub>4</sub>NaO<sub>8</sub>S Requires: C = 44.5%, H = 3.3%, N = 12.2%.

Found: C = 44.6%, H = 3.9%, N = 11.8%.

## Testing Example

Preparation of Dispersion 1

Compound A (0.1g) was dissolved in water (90g) using a magnetic stirrer, and a commercial sample of Pigment Yellow 74 (10g) (available under the trade name Hansa<sup>(R)</sup> Brilliant Yellow 5GX03) was added while stirring. Once this had wetted out the composition was transferred to a Silverson mixer and mixed for 10minutes at *ca* 7200rpm while the dispersing properties were observed. After a further 10minutes mixing the composition was transferred to a M110-F Microfluidiser and dispersed for 10minutes at 13000psi. Oversized particles were then removed by centrifugation at 3000rpm for 20 minutes to provide the final dispersion. The average particle size of the dispersion was determined using a Polymer Laboratories Light Scattering Photometer.

An ink was prepared from this dispersion by taking 17.5g of the dispersion and letting down to 50g by adding a mixture comprising by weight urea (5%), thiodiglycol (10%), polyethylene glycol 300 (10%), and water (75%).

Further inventive dispersions 2 - 4 and inks were prepared using the same procedure but with increased addition of compound A and with two levels of compound B as shown in Table 1 below. In all cases the pigments wetted and dispersed well. The particle size results are also shown in Table 1.

**Table 1**

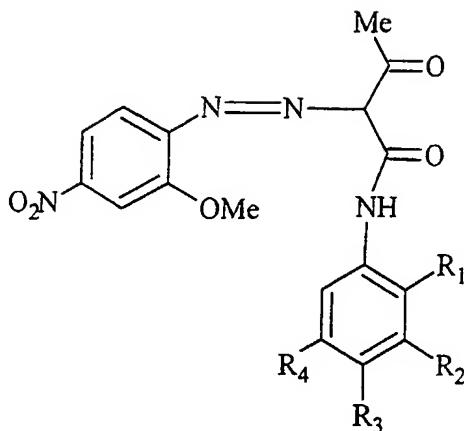
DISPERSION	Additive	Quantity	Particle size of dispersion	Particle size after 1 week at 70°
1 above	Compound A	0.1g	204nm	244nm
2	Compound A	0.3g	203nm	199nm
3	Compound B	0.1g	198nm	260nm
4	Compound B	0.3g	198nm	196nm

**Stability**

The stability of the dispersions and inks was assessed by storing samples in stoppered bottles in a water bath maintained at 70°. The samples were inspected after one week for any evidence of instability such as flocculation or settling-out. The particle size measured for the dispersions after one week at 70° is shown in Table 1. It is seen that the particle size of dispersions 1 and 3 using the lowest levels of additive has significantly increased, but that the measured particle size of dispersions 2 and 4 with higher, but still moderate addition has remained stable. It was found that the ink prepared from dispersion 1 destabilised after one day, but that all the other inks were stable. Despite the forcing conditions and the low concentration of the inventive compounds used, the dispersions and inks prepared at 3% ratio of additive to pigment thus have excellent storage stability.

Claims

1. A compound of general formula I



In which the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are individually hydrogen, a sulphonic acid group or salt thereof, a carboxylic acid group or salt thereof, a lower alkyl group, a halogen, a sulphonamide group, a carboxylic amide group, a nitro group, a group OX, or a group COOX where X is a lower alkyl group. By lower alkyl group is meant an alkyl group comprising up to four carbon atoms. At least one of the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is a sulphonic acid group or salt thereof.

2. A compound of formula I according to claim 1 wherein at least one of the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is a sulphonic acid group or salt thereof and the others of the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are hydrogen.

3. A compound of formula I according to either of claims 1 or 2 wherein at least one of the groups  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is a salt of a sulphonic acid group wherein the counter ion is selected from the group comprising lithium, sodium, potassium, an ammonium cation, or an organic nitrogen containing cation.
4. A pigment preparation which comprises a combination of at least one yellow pigment and at least one compound of formula I.
4. A pigment preparation according to claim 3 wherein the yellow pigment is CI Pigment Yellow 74.
5. An aqueous ink which comprises a combination of a yellow pigment and at least one compound of formula I.
6. An ink according to claim 5 wherein the yellow pigment is CI Pigment Yellow 74.
7. An ink according to claim 5 wherein the aqueous solvent comprises a combination of water and at least one water soluble organic cosolvent.



INVESTOR IN PEOPLE

Application No: GB 0016270.1  
Claims searched: 1-7 & 4bis

Examiner: Stephen Quick  
Date of search: 2 May 2001

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:	
UK Cl (Ed.S):	
Int Cl (Ed.7):	
Other:	Online: CAS ONLINE

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	No documents of relevance found	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**